β TITANIUM COMPOSITIONS AND METHODS OF MANUFACTURE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Application No. 10/609,003 filed on June 27, 2003 and to U.S. Provisional Application 60/392,620 filed June 27, 2002, the entire contents of which are incorporated herein by reference.

BACKGROUND

[0001] This disclosure relates to superelastic β titanium alloys, methods for manufacturing these alloys and articles derived therefrom.

[0002] Alloys that undergo a martensitic transformation may exhibit a "shape memory effect". As a result of this transformation, the high temperature phase known as "austenite" changes its crystalline structure through a diffusion-less shear process adopting a less symmetrical structure called 'martensite'. This process may be reversible as in shape memory alloys and therefore upon heating, the reverse transformation occurs. The starting temperature of the cooling or martensitic transformation is generally referred to as the M_s temperature and the finishing temperature is referred to as the M_f temperature. The starting and finishing temperatures of the reverse or austenitic transformation are referred to as A_s and A_f respectively.

[0003] At temperatures below the A_f, alloys undergoing a reversible martensitic phase transformation may be deformed in their high temperature austenitic phase through a stress-induced martensitic transformation as well as in their low temperature martensitic phase. These alloys generally recover their original shapes upon heating above the A_f temperature and are therefore called "shape memory alloys". At temperatures above the A_f, the stress-induced martensite is not stable and will revert back to austenite upon the release of deformation. The strain recovery associated with the reversion of stress-induced martensite back to austenite is generally referred to as "pseudoelasticity" or

1

"superelasticity" as defined in ASTM F2005, Standard Terminology for Nickel-Titanium Shape Memory Alloys. The two terms are used interchangeably to describe the ability of shape memory alloys to elastically recover large deformations without a significant amount of plasticity due to the mechanically induced crystalline phase change.

[0004] Nitinol is a shape memory alloy comprising a near-stoichiometric amount of nickel and titanium. When deforming pseudoelastic nitinol, the formation of stress-induced-martensite allows the strain of the alloy to increase at a relatively constant stress. Upon unloading, the reversion of the martensite back to austenite occurs at a constant, but different, stress. A typical stress-strain curve of pseudoelastic nitinol therefore exhibits both loading and unloading stress plateaus. However, since the stresses are different, these plateaus are not identical, which is indicative of the development of mechanical hysteresis in the nitinol. Deformations of about 8 to about 10% can thus be recovered in the pseudoelastic nitinol. Cold worked Nitinol also exhibits extended linear elasticity. Nitinol compositions, which display linear elasticity do not display any plateau but can recover a strain of up to 3.5%. This behavior is generally termed "Linear Superelasticity" to differentiate from transformation induced "Pseudoelasticity" or "Superelasticity". These properties generally make nitinol a widely used material in a number of applications, such as medical stents, guide wires, surgical devices, orthodontic appliances, cellular phone antenna wires as well as frames and other components for eye wear. However, nitinol is difficult to fabricate by forming and/or welding, which makes the manufacturing of articles from it expensive and time-consuming. Additionally, users of nickel containing products are sometimes allergic to nickel.

SUMMARY

[0005] In one embodiment, a composition comprises about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition.

[0006] In another embodiment, a composition comprises about 8.9 wt% molybdenum, about 3.03 wt% aluminum, about 1.95 wt% vanadium, about 3.86 wt% niobium, with the balance being titanium.

[0007] In yet another embodiment, a composition comprises about 9.34 wt% molybdenum, about 3.01 wt% aluminum, about 1.95 wt% vanadium, about 3.79 wt% niobium, with the balance being titanium.

[0008] In yet another embodiment, a method for making an article comprises cold working a shape from a composition comprising about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition; forming the shape; solution heat treating the shape; and cooling the shape.

[0009] In yet another embodiment, a method comprises cold working a wire having a composition comprising about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition; cold working the shape; and heat treating the shape.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a graphical representation showing the effect of molybdenum content on elastic recovery;

[0011] Figure 2 is a graphical representation of the effect of aging at 350°C on the elastic recovery of Sample 4 from Table 1;

[0012] Figure 3 is a graphical representation of the effect of aging at 350°C on the elastic recovery of Sample 5 from Table 1;

[0013] Figure 4 is a graphical representation showing the effect of aging at 350°C on the elastic recovery of Sample 6 from Table 1;

[0014] Figure 5 is a graphic representation showing the effect of aging at about 250 to about 550°C for 10 seconds on the elastic recovery of Sample 4 from Table 1;

[0015] Figure 6 is a graphic representation showing the effect of aging at about 250 to about 550°C for 10 seconds on the elastic recovery of Sample 5 from Table 1;

[0016] Figure 7 is a graphical representation showing the effect of cumulative cold drawing reduction on the UTS of Sample 11 from Table 2;

[0017] Figure 8 is a graphical representation showing the effect of cumulative cold drawing reduction on the Young's Modulus of Sample 11 from Table 2;

[0018] Figure 9 is a graphical representation showing the effect of tensile stress-strain curve for a wire having the composition of Sample 11 from Table 2 with 19.4% drawing reduction, tested to 2% strain;

[0019] Figure 10 is a graphical representation showing the effect of tensile stress-strain curve for a wire having the composition of Sample 11 from Table 2 with 19.4% drawing reduction, tested to 4% strain;

[0020] Figure 11 is an optical micrograph showing the microstructure of a cold drawn wire having the composition of Sample 10 from Table 2 with a 14% reduction;

[0021] Figure 12 is an optical micrograph showing partially recrystallized microstructure of a cold-drawn wire having the composition of Sample 10 from Table 2 having a 14% reduction after heat- treating at 816°C for 30 minutes;

[0022] Figure 13 is an optical micrograph showing fully recrystallized microstructure of a cold-drawn wire having the composition of Sample 10 from Table 2 having a 14% reduction after heat- treating at 871°C for 30 minutes;

[0023] Figure 14 is an optical micrograph showing the microstructure of a betatized Sample 10 from Table 2 after aging at 816°C for 30 minutes;

[0024] Figure 15 is an optical micrograph showing the microstructure of a betatized Sample 10 from Table 2 after aging at 788°C for 30 minutes;

[0025] Figure 16 is a graphical representation showing the UTS of betatized Sample 10 from Table 2 after aging at 500-900°C for 30 minutes;

[0026] Figure 17 is a graphical representation showing the ductility of betatized Sample 10 from Table 2 after aging at 500-900°C for 30 minutes;

[0027] Figure 18 is a graphical representation showing a tensile stress-strain curve tested to 4% tensile strain of a wire having the composition of Sample 11 from Table 2 after strand annealing at 871°C; and

[0028] Figure 19 is an optical micrograph showing the microstructure of a wire having the composition of Sample 11 from Table 2 after strand annealing at 871°C.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0029] Disclosed herein is a β titanium alloy composition having pseudoelastic properties and linear-superelastic properties that can be used for medical, dental, sporting good and eyewear frame applications. In one embodiment, the β titanium alloy composition has linear elastic properties and/or pseudoelastic properties after solution treatment. In another embodiment, the β titanium alloy composition has pseudoelastic properties that are improved with heat treatment. In yet another embodiment, the β titanium alloy composition displays linear-superelastic properties after being cold worked. The composition advantageously can be welded to other metals and alloys. The articles manufactured from the β titanium alloy can also be deformed into various shapes at ambient temperature and generally retain the high spring back characteristics

associated with superelasticity. It is to be noted that all ranges disclosed herein are inclusive and combinable.

[0030] Pure titanium has an isomorphous transformation temperature at 882°C. The body centered cubic (bcc) structure, which is called β-titanium, is stable above the isomorphous transformation temperature, and the hexagonal close packed (hcp) structure, which is called α titanium is generally stable below this temperature. When titanium is alloyed with elements such as vanadium, molybdenum, and/or niobium, the resulting alloys have an increased β phase stability at temperatures less than or equal to about 882°C (β transus temperature). On the other hand, when alloyed with elements such as aluminum or oxygen, the temperature range of the stable α phase is increased above the isomorphous transformation temperature. Elements which have the effect of increasing the β phase temperature range are called the β stabilizers, while those capable of extending the α phase temperature range are called the α stabilizers.

[0031] Unalloyed titanium transforms allotropically from body-center-cubic (bcc) β phase to hexagonal-close-packed (hcp) α phase upon cooling through the β transus temperature of 882°C. Depending on the alloying composition and thermo-mechanical processing, the ultimate microstructure of titanium alloys may have α, α+β, or β phases. The so-called β alloys contain critical amounts of β-stabilizing elements and exhibit extended β stability at high temperatures and a reduction in β transus temperature to lower temperatures as elemental concentration increases. When a certain concentration level is achieved, the β phase can be retained upon rapid cooling from the beta phase field, although it is metastable. The metastable β titanium alloys may undergo lattice transformations such as martensitic transformation under applied stress. Hence, titanium alloys at critical range of β stability may exhibit shape memory effect and superelasticity. The β-stabilizing elements are further classified into β -isomorphous groups and β-eutectoid groups. β-isomorphous elements such as V, Zr, Hf, Nb, Ta, Mo and Re stabilize the β phase by forming a simple β→α transformation while β-eutectoid elements

such as Cr, Mn, Fe, Co, Ni, Cu, Pd, Ag, W, Pt and Au stabilize the β phase by forming β→α+γ transformations.

[0032] Titanium alloys having a high enough concentration of β stabilizers, generally are sufficiently stable to have a meta-stable β phase structure at room temperature. The alloys showing such a property are called β titanium alloys. Martensite transformations are generally present in β titanium alloys. The martensitic transformation temperature in β titanium alloys generally decreases with an increasing amount of β stabilizer in the alloy, while increasing the amount of α stabilizer generally raises the martensitic transformation temperature. Therefore, depending on the extent of stabilization, β titanium alloys may exhibit a martensitic transformation when cooled rapidly from temperatures greater than those at which the β phase is the single phase at equilibrium.

[0033] The β titanium alloy generally comprises an amount of about 8 to about 10 wt% of molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium. All weight percents are based on the total weight of the alloy. Within the aforementioned range for molybdenum, it is generally desirable to have an amount of greater than or equal to about 8.5, preferably greater than or equal to about 9.0, and more preferably greater than or equal to about 9.2 wt% molybdenum. Also desirable within this range is an amount of less than or equal to about 9.9, preferably less than or equal to about 9.8, preferably less than or equal to about 9.75, preferably less than or equal to about 9.65, and more preferably less than or equal to about 9.5 wt% molybdenum, based on the total weight of the alloy.

[0034] Within the aforementioned range for aluminum, it is generally desirable to have an amount of greater than or equal to about 2.85, preferably greater than or equal to about 2.9, and more preferably greater than or equal to about 2.93 wt% aluminum. Also desirable within this range is an amount of less than or equal to about 5.0, preferably less than or equal to about 4.5, and more preferably less than or equal to about 4.0 wt% aluminum, based on the total weight of the alloy.

7

[0035] Within the aforementioned range for niobium, it is generally desirable to have an amount of greater than or equal to about 2, preferably greater than or equal to about 3, and more preferably greater than or equal to about 3.5 wt% niobium, based on the total weight of the alloy.

[0036] In one exemplary embodiment, it is generally desirable for the β titanium alloy to comprise 8.9 wt% molybdenum, 3.03 wt% aluminum, 1.95 wt% vanadium, 3.86 wt% niobium, with the balance being titanium.

[0037] In another exemplary embodiment, it is generally desirable for the β titanium alloy to comprise 9.34 wt% molybdenum, 3.01 wt% aluminum, 1.95 wt% vanadium, 3.79 wt% niobium, with the balance being titanium.

[0038] In one embodiment, the β titanium alloy may be solution treated and/or thermally aged. In solution treating the β titanium alloy, the alloy is subjected to a temperature greater than or equal to about 850°C, the β transus temperature for the alloy. The solution treatment of the alloy is normally carried out in either vacuum or inert gas environment at a temperature of about 850 to about 1000°C, preferably about 850 to about 900°C, for about 1 minute or longer in duration depending on the mass of the part. The heating is followed by a rapid cooling at a rate greater than or equal to about 5°C/second, preferably greater than or equal to about 25°C/second, and more preferably greater than or equal to about 50°C/second, by using an inert gas quench or air cooling to retain a fully recrystallized single phase β grain structure. In some instances, it is preferred that the quenched alloy is subsequently subjected to an ageing treatment at about 350 to about 550°C for about 10 seconds to about 30 minutes to adjust the amount of a fine precipitate of the ω phase. In another embodiment, the alloy may be subsequently subjected to an ageing treatment for up to about 8 hours at a temperature of about 350 to about 550°C.

[0039] In another embodiment, the β titanium alloy may be solution treated at a temperature below the β transus temperature of about 750 to about 850°C, preferably

about 800 to about 850°C, for about 1 to about 30 minutes to induce a small amount of α precipitates in the recrystallized β matrix. The amount of the α precipitates is preferably less than or equal to about 15 volume percent and more preferably less than or equal to about 10 volume percent, based on the total volume of the composition. This improves the tensile strength to an amount of greater than or equal to about 140,000 pounds per square inch (9,846 kilogram/square centimeter).

[0040] The β titanium alloy in the solution treated condition may exhibit pseudoelasticity. The solution treated β titanium alloy generally exhibits a pseudoelastic recovery of greater than or equal to about 75% of the initial strain when elastically deformed to a 2% initial strain, and greater than or equal to about 50% of the initial strain when elastically deformed to a 4% initial strain. The initial strain is the ratio of the change in length to the original length of the alloy composition.

[0041] The β titanium alloy in the solution treated condition may exhibit linear elasticity. The solution treated β titanium alloy generally exhibits a linear elastic recovery of greater than or equal to about 75% of the initial strain when elastically deformed to a 2% initial strain, and greater than or equal to about 50% of the initial strain when elastically deformed to a 4% initial strain. The initial strain is the ratio of the change in length to the original length of the alloy composition.

[0042] The β titanium alloy may be hot worked or cold worked. The β titanium alloy may be cold worked by processes such as cold rolling, drawing, swaging, pressing, and the like, at ambient temperatures. The β titanium alloy may preferably be cold worked to an amount of about 5 to about 85% as measured by the reduction in cross-sectional area based upon the original cross sectional area. Within this range it is desirable to have a cross sectional area reduction of greater than or equal to about 10, preferably greater than or equal to about 15% of the initial cross sectional area. Also desirable within this range is a reduction in cross sectional area of less than or equal to about 50, more preferably less than or equal to about 30% based on the initial cross-

sectional area. The β titanium alloy in the cold worked state (also referred to as the work hardened state) exhibits linear superelasticity where greater than or equal to about 75% of the initial strain is elastically recoverable after deforming to a 2% initial strain, and greater than or equal to about 50% of the initial strain is elastically recoverable after deforming to a 4% initial strain. In one exemplary embodiment related to cold working, the elastic modulus of the β titanium alloy is reduced through cold working by an amount of greater than or equal to about 10, preferably greater than or equal to about 20 and more preferably greater than or equal to about 25% based upon the elastic modulus, after the alloy is heat treated.

[0043] It is generally desirable to use shape memory alloys having pseudo-elastic properties, and which are formable into complex shapes and geometries without the creation of cracks or fractures. In one embodiment, the β titanium alloy having linear elastic, linearly superelastic, pseudoelastic or superelastic properties may be used in the manufacturing of various articles of commerce. Suitable examples of such articles are eyewear frames, face inserts or heads for golf clubs, medical devices such as orthopedic prostheses, spinal correction devices, fixation devices for fracture management, vascular and non-vascular stents, minimally invasive surgical instruments, filters, baskets, forceps, graspers, orthodontic appliances such as dental implants, arch wires, drills and files, and a catheter introducer (guide wire).

[0044] The stability of the β phase can be expressed as the sum of the weighted averages of the elements that comprise the alloy, often known as the molybdenum equivalent ($Mo_{eq.}$). P. Bania, Beta Titanium Alloys in the 1990's, TMS, Warrendale, 1993, defines the $Mo_{eq.}$ in the following equation (1) as

$$Mo_{eq.} = 1.00Mo + 0.28Nb + 0.22Ta + 0.67V + 1.43Co + 1.60Cr + 0.77Cu + 2.90Fe + 1.54Mn + 1.11Ni + 0.44W - 1.00Al \qquad (1)$$

wherein Mo is molybdenum, Nb is niobium, Ta is tantalum, V is vanadium, Co is cobalt, Cr is chromium, Cu is copper, Fe is iron, Mn is manganese, Ni is nickel, W is tungsten

and Al is aluminum and wherein the respective chemical symbols represent the amounts of the respective elements in weight percent based on the total weight of the alloy. It is to be noted that aluminum can be substituted by gallium, carbon, germanium or boron.

[0045] Hf (hafnium), Sn (tin) and Zr (zirconium) exhibit similarly weak effects on the β stability. Although they act to lower the β transus, these elements are considered neutral additions. US Air Force Technical Report AFML-TR-75-41 has suggested that Zr has a small Mo equivalent of 0.25 while Al is an α stabilizer having a reverse effect to that of Mo. Hence, the Mo equivalent in weight percent is calculated according to the following equation (2) which is a modified form of the equation (1):

$$Mo_{eq.} = 1.00Mo + 0.28Nb + 0.22Ta + 0.67V + 1.43Co + 1.60Cr + 0.77Cu + 2.90Fe + 1.54Mn + 1.11Ni + 0.44W + 0.25(Sn + Zr + Hf) - 1.00Al \qquad (2)$$

[0046] In general it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 7 to about 11 wt%, based upon the total weight of the alloy. In one embodiment, it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 7.5 to about 10.5 wt%, based upon the total weight of the alloy. In another embodiment, it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 8 to about 10 wt%, based upon the total weight of the alloy. In yet another embodiment, it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 8.5 to about 9.8 wt%, based upon the total weight of the alloy.

[0047] In one embodiment, in the equations (1) and (2) above, all of the elements may be optional if desired. In another embodiment, the elements that may be present in the composition in addition to titanium are molybdenum, vanadium, chromium, aluminum, and/or niobium. In another embodiment, it is generally desirable for the elements represented in equations (2) to be present in the composition in amounts of

11

greater than or equal to about 0.1, preferably greater than or equal to about 0.5, preferably greater than or equal to about 1, preferably greater than or equal to about 1.5, preferably greater than or equal to about 5, and preferably greater than or equal to about 10 wt%, based upon the total weight of the alloy composition. In yet another embodiment, it is generally desirable for the elements represented in equation (2) to be present in the composition in amounts of less than or equal to about 50, preferably less than or equal to about 40, preferably less than or equal to about 30, preferably less than or equal to about 28, preferably less than or equal to about 25, and preferably less than or equal to about 23 wt%, based upon the total weight of the alloy composition.

[0048] The superelastic β titanium alloy generally provides an adequate spring-back for eyewear applications. It is generally desired to use superelastic β titanium alloy having a minimum recovery of about 50% of the initial strain, when the alloy is deformed to an outer fiber initial strain of about 4% in a bend test. It is preferable to have a minimum recovery of greater than or equal to about 75% of the initial strain when the alloy composition is deformed to about 4% of the outer fiber initial length in a bend test. It is also generally desirable for the superelastic β titanium alloy to have a minimum recoverable strain of about 50% of the initial strain, when the alloy composition is strained to about 4% initial tensile strain. It is preferable to have a minimum recovery of greater than or equal to about 75% of the initial tensile strain, when the alloy is strained to about 4% initial strain in a tensile test. The strain recovery is measured as a function of the initial bending strain and the initial bending strain is expressed as a percentage of the ratio of the change in length to the original length.

[0049] The following examples, which are meant to be exemplary, not limiting, illustrate some of the various embodiments of the β titanium alloy compositions described herein.

EXAMPLES

EXAMPLE 1

[0050] All of the sample alloys discussed below were prepared by a double vacuum arc melting technique. The ingots were hot rolled and flattened to sheets having a thickness of 1.5 millimeter (mm). The sheets were then heat treated at 870°C for 30 minutes in air and air cooled to ambient temperature. Oxides on the sheets were removed by double-disc grinding and lapping to a thickness of 1.3 mm. Heat aging experiments were conducted at 350°C using a nitride/nitrate salt bath.

[0051] Permanent deformation and pseudo-elastic recovery strains were determined using bend tests. Specimens having dimensions 0.51 mm x 1.27 mm x 51 mm were cut from the sheets. The specimens were bent against a rod of approximately 12.2 mm in diameter to form a "U" shape to yield an outer fiber or outer surface strain close to 4%. The angles between the straight portions were measured afterwards and the strain recovery calculated by using the formula:

$$e(rec) = e\,(180\text{-}a)/180;$$

where "a" is the unrecovered angle and *"e'* is the outer-fiber bending strain.

[0052] Tensile strain recovery was measured by tensile elongation to a strain of 4% followed by unloading to zero stress. Tensile specimens with a cross sectional dimension of 0.90 mm x 2.0 mm were used and the strain was monitored using an extensometer. An environmental chamber with electrical heating and CO_2 cooling capabilities provided a testing capability from -30°C to 180°C.

[0053] Nine β titanium alloys having the compositions listed in Table 1 were examined. The percentage of the elastic recovery strain with respect to the total bend strain was measured for comparison.

Table 1

Sample #	Titanium	Molybdenum	Niobium	Vanadium	Aluminum
1	Balance	7.63	3.98	2.05	3.10
2	Balance	8.03	3.89	2.03	3.09
3	Balance	8.40	3.83	1.94	3.03
4	Balance	8.97	3.86	1.95	3.03
5	Balance	9.34	3.79	1.95	3.01
6	Balance	10.35	3.83	1.99	3.02
7	Balance	10.83	3.88	2.01	3.02
8	Balance	11.48	4.00	2.04	3.15
9	Balance	11.68	3.89	1.98	3.07

[0054] In the Table 1 above Sample 1 and Samples 6 – 9 are comparative examples. The results of elastic recovery after bending to approximately 4% outer fiber strain is graphically demonstrated in Figure 1. The figure shows a maximum elastic strain recovery at about 9 wt% molybdenum, where the alloy after solution heat treatment and subsequent air cooling, exhibits an elastic recovery strain of approximately 80% of the applied 4% deformation strain. Increasing or decreasing the molybdenum content from 9 wt% generally results in decreasing elastic recovery. It may also be seen that an aging treatment at 350°C for a short duration of 10 seconds results in an improved elastic recovery, for titanium alloys having a molybdenum content between 8.4 and 11 wt%. The optimal elastic strain recovery after heat aging at 350°C for 10 seconds for the alloy having about 9 wt% molybdenum is approximately 90% of the applied 4% bend strain. Alloys with a molybdenum content less than 8.4 wt% exhibit a different aging

characteristic. Aging at 350°C may degrade elastic strain recovery as for alloy 2 having about 8.03 wt% molybdenum, or has no significant effect as for alloy 1 having about 7.63 wt% molybdenum.

[0055] The percent of the elastic recovery to the total deformation during thermal aging at 350°C for Samples 4, 5 and 6 respectively, are plotted in the Figures 2, 3 and 4 respectively. From the Figures 2, 3 and 4 it may be seen that the elastic recoveries of all three alloys reach a maximum after aging for about 10 to about 60 seconds. Aging beyond 15 minutes (900 seconds) degrades the elastic recovery.

[0056] The percents of the elastic recovery to the total deformation during thermal aging at about 250 to about 550°C for 10 seconds for Samples 4 and 5 respectively are plotted in the Figures 5 and 6, respectively. An optimal for Sample 4 appears at 350°C, which improves the elastic recovery to a percentage close to 90% while aging at temperatures equal to or higher than 400°C degrade elastic recovery to about 40%. For Sample 5, aging in this temperature range generally improves the elastic recovery. The maximum improvement occurs at about 450°C where the elastic recovery is improved to 90%.

[0057] The alloys shown in Table I also exhibit linear superelasticity after cold working with a reduction of greater than or equal to about 30% in the cross-sectional area. For example, a wire fabricated from an ingot having a composition of 11.06 wt% molybdenum, 3.80 wt% niobium, 1.97 wt% vanadium, 3.07 wt% aluminum with the remainder being titanium exhibited an elastic recovery strain of 3.5% after bending to a total deformation of 4% outer fiber strain, when the reduction in the cross sectional area after cold working was 84%.

EXAMPLE 2

[0058] In this example, the β titanium alloys were manufactured by double vacuum arc melting. Chemistries of the alloys were analyzed using inductively coupled

15

plasma optical emission spectrometry (ICP-OE). The results are tabulated in Table 2. The ingot was hot-forged, hot-rolled and finally cold-drawn to wire of various diameters in the range of about 0.4 to about 5 mm. Inter-pass annealing between cold reductions was carried out at 870°C in a vacuum furnace for wires having a diameter of larger than 2.5 mm or by strand annealing under inert atmosphere for the smaller diameters. Tensile properties were determined using an Instron model 5565 material testing machine equipped with an extensometer of 12.5 mm gage length. Microstructures were studies by optical metallography using a Nikon Epiphot inverted metallurgical microscope.

Table 2

Sample #	Titanium	Molybdenum	Niobium	Vanadium	Aluminum	Mo_{Eq}
10	Balance	11.06	3.80	1.97	3.07	10.37
11	Balance	9.59	3.98	1.99	3.13	8.91

[0059] The strand-annealed wires generally have a higher ultimate tensile strength (UTS) around 1055 mega Pascals (MPa) than vacuum annealed wires and sheets, the typical UTS of which is about 830 MPa. Figure 7 plots the UTS of wires drawn from an annealed 1.0 mm diameter Sample 11 wire stock as a function of reduction in cross-section area. After a 49% reduction, the UTS was elevated from 1055 MPa to only 1172 MPa indicating a fairly weak strain hardening effect. Young's Modulus was determined by tensile testing the wire to 1% strain and measuring the linear slope of the stress-strain curve. As shown in Figure 8, cold-drawn wires generally have a lower modulus than does annealed wire. The modulus, of approximately 65.9 gigapascals (GPa) for the annealed wire, decreases with increasing accumulative amount of reduction and stabilizes at approximately 50 GPa after cold drawing with a cumulative reduction greater than 20%.

[0060] Similar to alloys in Table 1, Samples 10 and 11 exhibit linear superelasticity after cold working. Loading and unloading stress-strain curves tested to 2% and 4% tensile strains of a cold drawn, 0.91 mm diameter wire of Sample 11 with a

16

19.4% reduction are plotted in Figures 9 and 10, respectively. As may be seen in Figure 7, after unloading, following a 2% tensile elongation, the wire recovers the majority of the deformation leaving only a small plastic deformation of 0.1% strain. When deformed to a 4% tensile elongation, the residual strain after unloading increases to 1.4%. The wire recovers a strain of 2.6%. The residual strain decreases with increasing drawing (cross-sectional area) reduction. However, when the reduction exceeds 20%, specimens failed before reaching a 4% tensile elongation. As this data suggests, cold drawn β titanium alloy wires exhibit linear superelasticity and are capable of recovering large deformations greater than the typical elastic limit for conventional metallic alloys. The mechanical property of cold-drawn wire appears to be insensitive to chemical composition as the cold-drawn Sample 10 exhibits similar mechanical properties. All the loading/unloading tensile test results for Sample 10 are tabulated in Tables 3.

Table 3.

Cold Work Amount (%)	21	37	50	61	69
Tested to 2% tensile strain					
Elastic Strain (%)	1.9	1.8	1.8	1.9	2.0
Plastic Strain (%)	0.1	0.2	0.2	0.1	0.0
Tested to 3% tensile strain					
Elastic Strain (%)	2.5	2.6	2.6	2.7	2.7
Plastic Strain (%)	0.5	0.4	0.4	0.3	0.3
Tested to 4% tensile strain					
Elastic Strain (%)	---	2.8	2.9	3.1	3.2
Plastic Strain (%)	---	1.2	1.1	0.9	0.8

[0061] A micrograph in Figure 11 reveals the cold-worked microstructure of the Sample 10 wire after a 14% cold working reduction in cross sectional area. The recrystallized microstructures of the wire after heat-treatments at 816°C and 871°C for 30 minutes are shown in Figures 12 and 13, respectively. It is apparent that the material was

not fully betatized after the heat-treatment at 816°C as α phase was present in the microstructure. As may be seen in Figure 11, a fully recrystallized β grain structure was obtained after the heat-treatment at 871°C for 30 minutes.

[0062] Sample 10 wires hot-rolled to 8.6 mm in diameter were further drawn down to 6.0 mm diameter. After being fully betatized at 871°C for 30 minutes the 6.0 mm diameter wires were again aged at temperatures of about 500 to about 850°C for 30 minutes. As can be seen in Figure 14, the β structure was preserved after aging at 816°C. When the aging temperature was lowered to 788°C, intragranular α-phase precipitates began to appear in the microstructure as may be seen in Figure 15. The amount of intragranular α-phase precipitate increased with decreasing aging temperature. α-phase precipitates eventually appeared along the grain boundary when aged at 649°C and below.

[0063] The ultimate tensile strength (UTS) and tensile ductility (% reduction in cross-section area) of betatized Sample 10 from Table 2 after aging at a temperature of about 500 to about 900°C for 30 minutes are plotted in Figures 16 and 17, respectively. Fully betatized specimens such as solution-treated specimens and those aged at 816°C and above, exhibited a low UTS of about 800 MPa and a good tensile ductility of about 25 to about 30% in reduction in cross-section area (RA). As the aging temperature decreased, there was a drastic increase in UTS with a significant reduction in tensile ductility, presumably due to an increasing amount of α-precipitates. The peak of 1400 MPa in UTS coincides with the low in ductility (5% RA) and both appeared at approximately 500°C of aging temperature.

[0064] The Sample 11 composition in solution treated condition exhibits pseudoelasticity. Their mechanical properties are highly sensitive to solution heat treatment and subsequent aging at a temperature of about 350 to about 550°C. It was discovered that Sample 11 wires after strand annealing at 870°C exhibit well-defined pseudoelasticity. An example is presented in Figure 18, which shows a 4% tensile stress-

18

strain curve of a strand-annealed, 0.4mm diameter Sample 11 wire. After deforming to a 4% elongation, the wire specimen was able to go through a pseudoelastic recovery recovering a 3.4% tensile strain and leaving a residual strain of only 0.6% after unloading.

[0065] A transverse cross-sectional view of the wire microstructure is shown in a micrograph of Figure 19. Instead of the anticipated β structure, the microstructure consists of equiaxial α precipitates in β matrix. It appears that the short duration of strand annealing did not allow the wire to fully recrystallize into the β grain structure. Without being limited by theory, it is believed that this may explain why strand-annealed wire generally has a higher UTS when compared to that of a fully betatized material.

[0066] As may be seen from the above experiments, the β titanium alloys can display an elastic strain recovery of 88.5%, when subjected to an initial bending strain of 4%. The strain recovery is measured as a function of the initial bending strain and the initial bending strain is expressed as a percentage of the ratio of the change in length to the original length. These alloys may be advantageously used in a number of commercial applications s uch as e yewear f rames, f ace i nsert a nd h eads for golf c lubs, o rthodontic arch wires, orthopedic prostheses and fracture fixation devices, spinal fusion and scoliosis correction instruments, stents, a catheter introducer (guide wire) and the like.

[0067] While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention.